CHAPTER II

MATERIALS AND METHODS
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MATERIALS

Acid amides containing various electron releasing and electron attracting groups or atoms and textile cross-linking agents such as ethyleneurea (EU) and dihydroxyethyleneurea (DHEU), considered as standards of reference in this study, were synthesized in the laboratory. Along with their physical properties and analysis, these compounds are listed in Table No. 4 in Chapter III (page 101). The purity of the amides, as calculated from their analyses, was of the order of 97 to 100%.

Chromotropie acid, copper sulphate, potassium sulphate, sulfuric acid, fuming nitric acid, silver nitrate and other chemicals which were used for quantitative analysis were of Analar grade.

Other reagents used for organic synthesis, kinetic study and cross-linking treatment of cotton cellulose such as magnesium chloride hexahydrate, citric acid, formaldehyde, acetic acid, triethyl amine etc. were of reagent grade.

The fabric used for evaluation of the organic chemical finishes was a white, desized, scoured, bleached and mercerized cotton poplin (36s/36s; 120/64) weighing 105 gm. per square yard.
METHODS

Characterization and Analysis of Compounds Synthesized

(A) Melting Point:
Melting points of amides were determined in thin-walled capillaries and are uncorrected.

(B) Nitrogen Estimation of Acid Amides:
About 10 mg. of sample (or enough to require several milliliters of 0.01N sulfuric acid in the titration of the distilled ammonia) was weighed into a Kjeldahl flask. To the flask were added 0.9 gm. potassium sulfate, 0.1 gm. copper sulfate and 5 ml. of concentrated sulfuric acid (sp. gr. 1.84) and the mixture was boiled for three to four hours. After the completion of the digestion, the digest was subjected to distillation as described below:

The digest was poured into the inner chamber of distillation flask, through the funnel. A 250 ml. Erlenmeyer's flask containing 25 ml. of 0.01N sulfuric acid with 4-5 drops of the mixed indicator (methylene blue and methyl red 1:2 in alcohol), was placed under delivery tube of the condenser, so that the tip was well immersed in the liquid. A rapid flow of steam was run. Into the distillation chamber 50% alkali (NaOH) solution was carefully run till the colour of the solution inside the chamber turned from blue to brown. The steam was passed further 7 minutes and then the flask containing the acid was lowered and steam was passed for two to three minutes to wash the water condenser. The washing from outside the
condenser, and tip, were also collected in the flask. The acid solution in the flask was titrated with 0.01N NaOH solution. The end point was indicated by the change in the colour of solution from blue to green. The nitrogen content was calculated as under:

\[
\text{Percent Nitrogen of compound} = \frac{\text{Titration value x 0.014 x Normality of alkali}}{\text{Wt. of compound in gm.}} \times \frac{100}{1}
\]

(C) Halogen Estimation of Acid Amides:

Five to 8 mg. of sample and 20 mg. of silver nitrate crystals were added to the Carius combustion tube. Six to seven tenths milliliters of fuming nitric acid (sp. gr. 1.49-1.50), was added while the tube was rotated to wash down any remaining particles. The Carius tube was immediately sealed and then heated in the Carius furnace for 7-8 hours at 250°. It was allowed to cool, the pressure released, and then cut as near to the top as possible. A few drops of water were added to dilute the nitric acid and this was followed, with cautious mixing, by enough water. It was then placed in a hot water or steam bath, protected from light, for about 20 minutes.

The precipitate was then transferred to the previously weighed filter tube. The washing, alternately with dilute nitric acid and ethanol was repeated several times to ensure complete transfer of the precipitate. The precipitate was finally washed with a little ethanol and sucked dry. The tube was then placed in an oven and the precipitate dried at 120°, for about 30 minutes. The tubes were then transferred to desiccator
and weighed after 45 minutes. Difference in weight represents the weight of silver halide.

Calculation: Factor. \( \frac{\text{Cl}}{\text{AgCl}} = 0.2474 \)

\( \frac{\text{Br}}{\text{AgBr}} = 0.4255 \) and \( \frac{\text{I}}{\text{AgI}} = 0.5405 \)

Percent Halogen = \( \frac{\text{Wt. precipitate} \times \text{Factor} \times 100}{\text{Wt. sample}} \)

(D) **Infra-red Spectra of Acid Amides:**

Paraffin Oil Paste Samples: The standard procedure for solid samples was to make a paste or suspension of the powdered sample in purified paraffin oil. The oil and solid sample were ground together in a cone-shaped glass mortar (capacity about 1 cc.) with a carefully fitted cone-shaped glass pestle. A five minute grinding period was usually sufficient. The paste when ground sufficiently was placed, with the aid of small spatula, along one edge of a salt plate. The cover salt plate was then slipped over it and squeezed down, spreading the paste layer evenly between the two plates. Paraffin layer and compound paste layer were made for running full spectrum on Perkin Elmer Infracord 137, a double beam spectrophotometer.

(E) **Nuclear Magnetic Resonance (NMR) Spectra:**

NMR spectra of such acid amides as formamide, acetamide, propionamide, butyramide, isobutyramide, trimethylacetamide, chloroacetamide, bromoacetamide and trichloroacetamide dissolved in D$_2$O were obtained on a Varian A60.D spectrometer. The NMR spectral conditions were:
Temperature: 36.5°C
Sweep time: 250 sec.
Resonance frequency: 60 MHz

The NMR spectra of 2,4,6-tribromophenoxyacetamide, 2,4,6-tribromophenoxy acetic acid and 2,4,5-trichlorophenoxy acetic acid dissolved in DMSO-d6/CDCl3 were obtained on a 100 MHz NMR spectrometer. The NMR spectral condition were:

Temperature: 36°C
Sweep time: 500 sec.
Resonance frequency: 100 MHz

Chemical shifts are expressed in value using tetramethylsilane as an internal standard.

(F) Neutralization Equivalent:
Neutralization equivalent of 2,4,5-trichlorophenoxy acetic acid and 2,4,6-tribromophenoxy acetic acid was determined by titrating their known weight with standard sodium hydroxide solution according to the following procedure:

About 1.0 gm of the sample was weighed accurately into each of three 250 ml Erlenmeyer flasks. To each flask, approximately 25 ml of absolute ethanol was added to dissolve the solid. This was then titrated with the standard carbonate-free sodium hydroxide until the solution acquired a faint pink colour. Phenolphthalein being used as indicator. Volume of sodium hydroxide in milliliters was noted. Since the two acids under assy were monobasic, the neutralization equivalent was calculated
as shown below:

\[ \frac{W \times 1000}{N_x} = \text{Neutralization equivalent} \]

(G) Calibration Curve for Formaldehyde Estimation by Chromotropic Acid Method:

(a) Preparation of 15% Formaldehyde Solution:
Equal quantities of paraformaldehyde (50 gm.) and water were refluxed with 10 ml. of 2N sulfuric acid in a two-necked 250 ml. round bottomed flask until a clear solution was obtained. The solution was then steam distilled and 250 ml. of distillate was collected; keeping at approximately constant volume of solution in round bottomed flask. The distillate (250 ml.) was approximately 15% formaldehyde solution.

(b) Determination of Formaldehyde with 5,5-Dimethylcyclohexanedione-1,3:
A solution containing approximately 1 gm. per liter of formaldehyde was prepared by appropriate dilution of 15% formaldehyde solution. This solution was standardized by the method of sodium sulphite, a 10 ml. sample being taken for the standardization. Assuming that 10 ml. of the solution contained 10 mg. of formaldehyde, the sample would require 0.107 gm. of dimedon for a 15% excess two molecules of dimedon condense with one mole of formaldehyde through loss of a molecule of water.

Two 10 ml. samples of the formaldehyde solution were withdrawn and each was added to 0.107 gm. of dimedon dissolve in 50 ml.
of water. The mixtures were shaken, allowed to stand overnight in stoppered flasks, and filtered through previously weighed sintered-glass crucibles. The precipitates and crucibles were dried in vacuum over phosphorus pentoxide to constant weight, and multiplication of weight of precipitate by 0.1027 (ratio of molecular weights) of formaldehyde to dimedon gave the amount of formaldehyde in the 10 ml. samples.

The requisite solution for the construction of the curve being obtained by accurate dilution of a formaldehyde solution standardized by dimedon. Various volume (1-ml to 5-ml) of this diluted solution was transferred to a 6" x 1" boiling tube, volume of the each solution adjusted to 5 ml. by addition of distilled water. After addition of 1.0 ml. of 5% chromotropic acid and 5 ml. of concentrated sulfuric acid, the contents were mixed by shaking the tube, which was then placed for 30 minutes with the lower half submerged in boiling water. The solution was (pink to deep ruby red in colour) allowed to cool, then transferred to a 100 ml. volumetric flask, again cooled, and finally adjusted to volume.

The intensity of the colour of the final solution, expressed as optical density, was measured at 570 n.m. by means of "Spectronic 20". Optical density versus microgram of formaldehyde was plotted and a straight line obtained is shown in Fig. No.3.

(H) Fabric Treatment:
Prior to finishing treatment the fabric was soaked in 0.5 percent
Fig. 3: Calibration curve for formaldehyde.
acetic acid solution for 30 minutes keeping the fabric to liquor ratio 1:50. The fabric was then squeezed in a laboratory mangle and air-dried. This treatment was given in order to remove the alkali or alkaline salt contaminants which might poison the acidic catalyst, generally used for curing.

After completion of methylolation of acid amides, the solution was made neutral by addition of dilute hydrochloric acid. In that solution required amount of magnesium chloride hexahydrate and citric acid for pH adjustment were added. Concentration of resin was adjusted by addition of distilled water. The resin solutions containing required catalyst were applied to the fabric with a laboratory mangle. The mangle pressure was adjusted to give approximately 100 percent wet pick up. The samples were then placed on pin frames at their original dimensions, dried at 60°C for 7 minutes and cured at 125°C for 10 minutes except in cases in which resins were found to be very sensitive to curing conditions and hence still milder conditions were employed.

The cured samples were then washed with a solution containing 2 gms. per litre non-ionic detergent and 1 gm. per litre soda, keeping material to liquor ratio 1:50 at 50°C for 30 minutes. The samples were then washed with fresh water and then finally dried.

(I) Bound Formaldehyde:
Bound formaldehyde in the treated fabric was estimated
spectrophotometrically by Roff's chromotropic acid method. 

About 0.1 gm. fabric sample, weighed accurately, was steeped in 100 ml. of 12N sulfuric acid for 24 hours at room temperature and 2 ml. of the extract was used for the estimation. Percent formaldehyde in the extract was estimated according to the method described earlier.

(J) **Bound Nitrogen:**

Bound nitrogen of the treated fabric was estimated by the Kjeldahl method. About 1 gm. fabric sample was weighed accurately, cut into small pieces, and digested with 20 ml. of concentrated Analar sulfuric acid, 10 gm. potassium sulphate and 0.5 gm. of copper sulphate for three to four hours after which period the solution was allowed to cool and then diluted to 100 ml. with distilled water. 25 ml. of the diluted solution was used for distillation. Percent nitrogen was estimated according to procedure (B).

(K) **Bound Halogen:**

Fabric treated with methylol haloacid amides were washed repeatedly with distilled water; dried and 0.1 gm. of bone dried fabric was placed in Carius tube along with nitric acid (0.8 ml.) and silvernitrate (20 mg.). The tube was sealed and then heated in the Carius furnace for 7-8 hours at 250°C. Percent halogen was estimated according to the procedure (C).

(L) **Infrared (IR) Spectra of Fabrics:**

The IR spectra of untreated and treated fabrics were obtained by the KBr disc method. A sample of 10 mg. of cotton fabric
was cut into small pieces. These were converted into powder in a mechanical vibrator-grinder-Wig-L-Bug amalgamator (Crescent Dental Manufacturing Co., Chicago, Illinois). About 2 mg. of the powder was mixed thoroughly with 200 mg. of KBr (200 mesh) and transparent KBr discs were prepared. IR spectra were obtained on a Perkin Elmer Infracord 137B, a double beam instrument.

(M) Insolubility in Cuprammonium Hydroxide: 195

Sufficient sample was weighed accurately so as to prepare exactly a 0.5% solution in cuprammonium hydroxide (15 gm/l. copper, 200 gm/l. ammonia) and placed in a centrifuge tube (vol. 45-50 ml.) which was then filled completely with cuprammonium solution. The sample weight was corrected for moisture, determined separately. Two small stainless steel balls (1/8 in. diameter) were introduced for stirring and the tube closed with a rubber stopper; care was taken to exclude air. The centrifuge tubes containing the different fabric samples were stirred overnight at 6 rpm in a rotating box which protected them from light. Next day, the tubes were centrifuged for 10 min. at 2700 rpm in a laboratory centrifuge and the supernatant liquid was decanted off. The tubes were refilled with fresh solvent and the entire procedure of centrifuging, and decanting off was repeated. The residue in the centrifuge tubes was washed successively with fresh cuprammonium solution, with 28% ammonia solution, and then with 20% acetic acid till free from colour. It was then filtered through a previously weighed sintered glass crucible
No. 3, washed thoroughly with distilled water, anhydrous ethyl alcohol and finally dried in an oven at 110°C for 3 hours. After being cooled and conditioned at 65% RH, the crucible with residue was weighed. (The moisture content of the residue was determined and necessary correction applied). The reported value of cuprammonium insolubility is the weight of the dry residue expressed on 100 gm. of bone dry fabric.

(N) Chlorine Damage:
The available chlorine in hypochlorite solution was estimated iodometrically as follows:

The original solution was diluted ten times with distilled water. To 10 ml. diluted solution in an Erlenmeyer flask, 5 ml. of 10% potassium iodide and 10 ml. of 10% acetic acid solution were added. The liberated iodine was then titrated against 0.1N sodium thiosulphate using starch as an indicator.

Prewetting: Fabric samples (14" warp and 8" weft) were wetted with distilled water keeping material to liquor ratio 1:50 at 7 pH and 71 ± 3°C temperature. After leaving the sample for three minutes it was removed from bath, allowed to drain and cooled to room temperature.

Test specimen were then transferred to a chlorinating solution, keeping material to liquor ratio 1:50, at 9.5 ± 0.1 pH and 25° ± 1°C for 15 minutes; specimens were then removed and allowed to drain momentarily. Treated samples were made chlorine free by giving repeatedly distilled water wash and were air dried. Ten ravelled strips were prepared and conditioned for 24 hours at 65% RH and 25°C temperature. Out of
10 strips, 5 strips were scorched at 185°C for 30 seconds and conditioned as mentioned above. The tensile strength of scorched and unscorched samples were determined. Using the following formula damage caused by retained chlorine was calculated:\textsuperscript{196}

$$\frac{T_c - T_{cs}}{T_c} \times 100 = \% \text{ Loss in Tensile Strength}$$

Where

- $T_c$ = Average tensile strength of chlorinated unscorched specimens;
- $T_{cs}$ = Average tensile strength of chlorinated scorched specimens.

(0) **Soil Burial Test:**\textsuperscript{197}

Cow dung manure and sandy loam field soil (1:1 w/w) were mixed well and sieved through a $\frac{3}{8}$ inch mesh screen. Moisture content of that soil was estimated. The test soil was placed in boxes (2' x 1' x 1') and brought to optimum moisture content (25 to 30\%) by gradual addition of water accompanied by mixing to avoid puddling. The moisture content was maintained to this level by covering the soil container with a suitable lid. Boxes were kept in a conditioned room at 65\% RH and 25 ± 2°C.

The test specimens were prepared by cutting fabric 6 x 1½ inch with the long dimension parallel to the warp and ravelling to exactly 1.0 inch width. Specimens were wetted by dipping in
water containing 0.05% of a nonionic wetting agent and placed (5 to 6 inch depth) horizontally in prepared soil. After the exposure of 7, 14 and 21 days to soil burial, the specimens were gently washed with water and air dried. Tensile strength of the conditioned sample was determined by ASTM method. Control fabric lost 90% tensile strength after seven days exposure.

(P) Determination of Stability of Methylolated Acid Amide Finisher Towards Acid Hydrolysis:
Finished fabric was hydrolyzed with 0.1N hydrocholoric acid at 66°C for 40 minutes, keeping material to liquor ratio 1:15. Fabric was then washed with tap water and dried at room temperature. Percent formaldehyde, nitrogen and insolubility in cuprammoniumhydroxide of hydrolyzed fabric were estimated according to procedure described earlier. Drop in crease recovery angle was determined by the ASTM method.

(Q) Dyeing with Procion Brilliant Red 2BS:
I. To 308 ml. water in 800 ml. beaker 20 ml. of 0.1% aqueous solution of dyestuff were added. 10 gm. of desized, mercerized and bleached poplin was placed into the solution for 10 minutes. 64 ml. of predissolved common salt (25% aqueous solution) was then added and dyeing continued for 30 minutes at 30°C temperature. After that 8 ml. of predissolved (10% aqueous solution) soda ash was added and dyeing was continued for 45 minutes at 30°C temperature.
After completion of dyeing, the fabrics were washed with running tap water and then with non-ionic detergent at 90°C for 15 minutes.

II. Fabric finished with N-methylol dimethylamino acetamide was dyed with the same dyestuff according to the following procedure.

To 375 ml. water in 800 ml. beaker 20 ml. of 0.1% aqueous solution of dyestuff was added. pH of the dyebath was adjusted to 3 by addition of glacial acetic acid. 10 gm. of fabric was placed into the dye solution kept at 30°C and the dyeing was continued for 45 minutes.

After 45 minutes, the dyed fabric was washed according to the process described above.

(R) Estimation of Dye on Fabric:

Hundred milligram dyed fabric was dissolved in 50 ml. cold 70% v/v concentrated sulfuric acid at 10°C and the intensity of the colour of the solution, expressed as optical density, was measured at 535 n.m by means of "spectronic 20". Microgram of dye on fabric was read from a previously determined calibration curve.

(S) Washfastness of Dyed Fabric:

One test piece 10 x 4 cm. was placed between two 10 x 4 cm. pieces of undyed cloth, and was sewn along four sides to form a composite specimen. Composite specimen with 10 stainless steel balls were placed in a container; necessary amount of soap-soda solution (5 gm./liter and 2 gm./liter) previously heated to 95°C ± 2°C was added to give a material to liquor
ratio of 1:50. Specimen was treated for 30 minutes by a suitable mechanical washing device which consisted of a water bath containing a rotor fastened to a shaft in which container of 500 ml. capacity were rotated, at a standard speed of 40 ± 2 rpm. The temperature of the water bath was thermostatically controlled to maintain the test solution at 95 ± 2°C. Specimen was removed after 30 minutes, washed with distilled water and tap water. The composite specimen was opened out and was dried in air. Evaluation of the treated test piece was done by the Indian Standards methods.200,201

(I) Colourfastness to Light:

Colourfastness to light was examined by carbon arc lamp202 fading apparatus (Fadometer Model - FDA 2). Dyed fabric (2¾ x 3¾ inch) was mounted on the specimen rack; supported both at the top and bottom in a proper vertical alignment. By the help of controls relative humidity of the air surrounding the specimen rack was adjusted to 30 ± 5 at 60 ± 3°C. Specimen were examined after exposure for periods of 3 and 5 hours. Rating was given by the help of International Geometric Gray Scale for colour change.

Physical Properties of Treated Fabric

(A) Dry and Wet Crease Recovery Angles:

Dry crease recovery angles of the conditioned samples were determined using the Monsanto tester and ASTM method.203 Wet crease recovery angles were determined by soaking the sample strips in water containing a non-ionic detergent, blotting
the samples to remove excess water and then measuring the recovery angle on the Monsanto tester.

(B) Tensile Strength:
Tensile strength of one inch wide ravelled strip of fabric was measured with a constant rate of traverse machine (2-5/8 inch per minute)\textsuperscript{204} using three inch gauge length.

(C) Tear Strength:
Tear strength was measured according to ASTM method.\textsuperscript{205}